

The use of Radon (Rn^{222}) isotopes to detect groundwater discharge in streams draining Table Mountain Group (TMG) aquifers

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Environmental isotopes have been used for decades as natural tracers in studies aimed at understanding complex hydrogeological processes such as groundwater and surface water interactions. Radon (Rn^{222}) is a naturally occurring, radioactive isotope which is produced from radium (Ra^{226}) during the radioactive decay series of uranium (U^{238}). Since U^{238} is present in most geological substrates, Rn^{222} is produced in various lithological structures and subsequently transported with groundwater through fractures and pore spaces in an aquifer towards surface water discharge points in rivers and springs. This study aimed to determine (i) the concentration of Rn^{222} within both surface water and groundwater in Table Mountain Group (TMG) aquifer systems, and (ii) the feasibility of using Rn^{222} isotopes as a natural tracer in groundwater-surface water interaction studies. This study was conducted in a highly fractured TMG aquifer system near Rawsonville, South Africa. Surface water from two perennial rivers (i.e. Gevonden and Molenaars), together with groundwater from a nearby borehole, were sampled and their corresponding Rn^{222} concentrations measured. Our study found median Rn^{222} concentrations in the Gevonden River of $76.4 \text{ Bq}\cdot\text{L}^{-1}$ and $67.2 \text{ Bq}\cdot\text{L}^{-1}$ in the dry and wet seasons, respectively. Nearly 12% of surface water samples exceeded $100 \text{ Bq}\cdot\text{L}^{-1}$. These abnormally high Rn^{222} concentrations can only be attributed to the influx of groundwater with extremely high Rn^{222} concentrations. Under ambient (no pumping) conditions, Rn^{222} concentrations in groundwater range between $130\text{--}270 \text{ Bq}\cdot\text{L}^{-1}$. However, when the borehole was pumped, and inflowing water from the surrounding aquifer was sampled, even higher Rn^{222} concentrations ($391\text{--}593 \text{ Bq}\cdot\text{L}^{-1}$) were measured. These extremely high Rn^{222} concentrations in groundwater are believed to be attributed to the underlying granitic geology and the prevalence of faults. The use of Rn^{222} isotopes as an environmental tracer in groundwater-surface water interaction studies is therefore regarded as a feasible option in similar highly fractured aquifer systems.

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INTRODUCTION

The interaction between surface water and groundwater is dynamic and complex (Sophocleous, 2002; Hunt et al., 2005). Understanding the linkages between groundwater and surface water bodies is critical for sustainable utilization and management of these complex systems. According to Wu et al. (2004), it is critical to establish the flow paths, patterns, water quantity and quality of the water flowing between surface water and groundwater, to develop and manage water resources efficiently. Since the properties of surface water and groundwater are usually chemically, physically and biologically different, the exchange of water between the two entities may have a significant impact on the water quality of either of these hydrological units (Kalbus et al., 2006).

Radioactive and stable isotopes have been applied as tracer techniques in many Earth systems studies world-wide (Thomas and Rose, 2003; Gibson et al., 2005; Kalbus et al., 2006; Praamsma et al., 2009). For roughly half a century, environmental isotopes have been used as natural tracers in studies aimed at understanding hydrogeological processes (Thomas and Rose, 2003). This field has developed in its scope and currently environmental isotopes are also used to study the exchange of water between groundwater and surface water sources (Midgley and Scott, 1994; Thomas and Rose, 2003; Wu et al., 2004). Other hydrological tracer studies include the application of stable isotopes such as ^{18}O and ^2H (e.g. Harrington et al., 2002; Hunt et al., 2005; Praamsma et al., 2009), as well as radioactive isotopes such as tritium (e.g. Scanlon, 2000), ^{14}C (e.g. Harrington et al., 2002) and radon (Rn^{222}) (e.g. Ellins et al., 1990; Kalbus et al., 2006; Moreno et al., 2014; Srinivasamoorthy et al., 2018).

Rn^{222} is a naturally occurring, odourless, radioactive noble gas with a half-life of 3.83 days (Ellins et al., 1990; Wu et al., 2004). Rn^{222} isotopes are daughters produced from radium (Ra^{226}) during the radioactive decay series of uranium (U^{238}) (Broecker et al., 1967; Schubert et al., 2008). Since U^{238} is present in most rocks and has a half-life of 4.5 billion years, Ra^{226} and Rn^{222} are readily available in geological substrates such as granites, carbonaceous shale and metamorphic rocks (Hoehn and Von Gunten, 1989; Ellins et al., 1990; Schubert et al., 2008; Moreno et al., 2014). Ra^{226} , and subsequently Rn^{222} concentrations, tend to increase along faults and fractures, particularly when aquifers have been exposed to tectonic activities (Ellins et al., 1990; King et al., 1996; Vogiannis et al., 2004). Therefore, the lithology of the aquifer material influences the concentration of Rn^{222} found in the aquifer. The radioactive decay of Ra^{226} alongside and within the aquifer is the principal means for the accumulation of Rn^{222} in groundwater, whereby the Rn^{222} gases continuously diffuse into the pore spaces of the aquifer resulting in Rn^{222} -enriched groundwater (Loomis, 1987; Hoehn and Von Gunten, 1989; Cecil and Green, 2000; Wu et al., 2004). Consequently, Rn^{222} concentrations are significantly

higher in groundwater than in surface water bodies, with rainfall containing no Rn^{222} . High Rn^{222} concentrations measured in surface water may therefore be indicative of groundwater influx into the surface water source.

The application of radioactive isotopes, such as Rn^{222} , in hydrogeological studies has been mostly limited to studies in Asia, Europe, North and South America (e.g. Loomis, 1987; Hoehn and Von Gunten, 1989; Almeida et al., 2004; Moreno et al., 2014; Singh et al., 2018). Our study is one of the first in South Africa using Rn^{222} as an environmental tracer in hydrogeological studies between groundwater and rivers. Other studies, such as Eilers et al. (2015), Masevhe et al. (2017) and Botha et al. (2019), quantified Rn^{222} concentrations in either surface water or groundwater (not both) in different parts of South Africa. The objective of this study is to determine (i) Rn^{222} concentrations within both surface water and groundwater, and (ii) the feasibility of using Rn^{222} isotopes as a natural tracer in groundwater-surface water interaction studies in Table Mountain Group (TMG) aquifer systems.

Study site

This study was conducted in the Rawsonville area ($33^{\circ} 42' 55'' \text{ S}$; $19^{\circ} 14' 48'' \text{ E}$) of the Western Cape, which is situated in the winter rainfall region of South Africa (Fig. 1). The area is characterized

by a Mediterranean climate with cold, wet winters and warm, dry summers. The mean annual precipitation (MAP) for the area is approximately 800 mm, most of which occurs between the months of June and August (Conradie, 1995). The vegetation type may be described as mountainous fynbos (Mucina and Rutherford, 2006). The surrounding geology in this area comprises mainly of highly fractured TMG sandstone forming part of the Cape Supergroup, with scattered granitic outcrops (Thamm and Johnson, 2006).

The Gevonden and Molenaars rivers were studied to determine the interaction between groundwater and these surface water bodies using Rn^{222} isotopes. The Gevonden River is a small, perennial headwater stream which flows along the Waterkloof Fault before its confluence with the Molenaars River. The Molenaars River is a major perennial river with its headwaters situated in the Klein Drakenstein Mountains. The Molenaars River eventually joins the Breede River just northeast of Rawsonville. During the dry summer months, the Gevonden River is characterized by a low stream stage but often floods its banks during the wet season, which is a common characteristic of many fynbos mountain rivers (Brown et al., 2004). A borehole (BH3) situated within 100 m of the Gevonden River was sampled to determine groundwater Rn^{222} concentrations under both ambient (no pumping) and pumping conditions between both wet and dry seasons (Fig. 2).

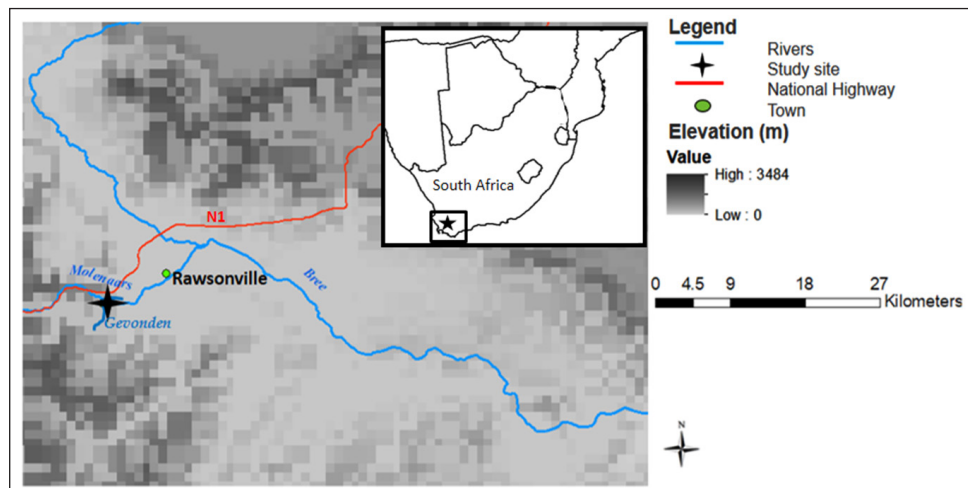


Figure 1. The study site location in relation to Rawsonville town and South Africa

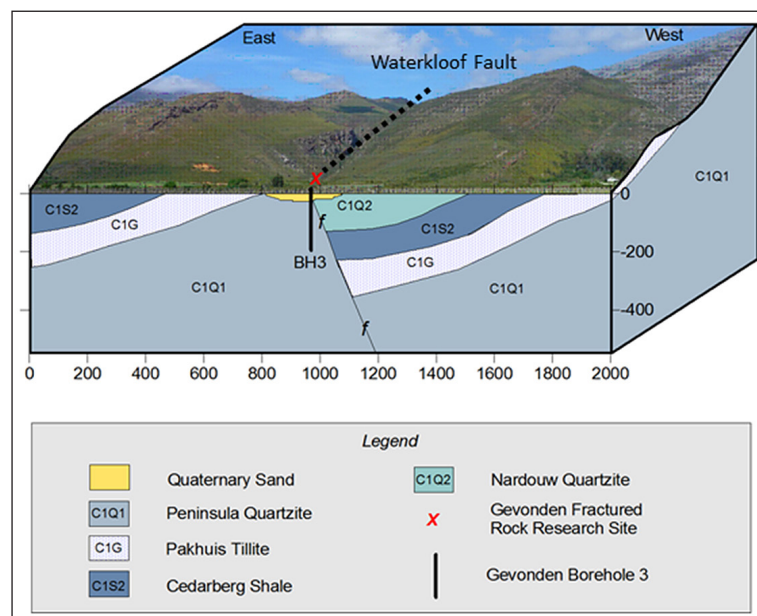


Figure 2. Conceptual geological cross-section for the Gevonden research site near Rawsonville

METHODS

Surface water samples ($n = 32$) were collected from the Gevonden and Molenaars rivers during both dry and wet seasons. Sampling points were randomly selected but also confined by accessibility constraints. Water samples were collected using 250 mL sample bottles, which were sealed under water to prevent Rn^{222} gases from escaping (Weaver et al., 2007). Samples were collected 15 cm below the water surface as to avoid the air-water interface where gaseous exchange would influence Rn^{222} concentrations (Ellins et al., 1990).

Groundwater samples were collected to represent various depths down the borehole profile (average of 25 m intervals) under both ambient conditions (i.e., no pumping) and pumping conditions (at 2 L/s pumping rate), with the use of a depth-specific sampler. This device is connected to a power source, and when lowered to a specific depth in the borehole a small pump displaces the water between two non-return valves and the sample is secured when the pump is switched off. Water was then carefully transferred into the plastic sample bottles.

The Rn^{222} concentrations were then analysed in a controlled laboratory environment using a RAD-7 electronic radon detector and RAD-H2O accessory (DurrIDGE Company, USA). This instrument is known to be very precise and capable of measuring concentrations as low as 1 mBq (Masevhe et al., 2017). Tests were conducted at normal room temperature with sufficient desiccant in the air sample path of the equipment (see Botha et al., 2019 for detailed protocol).

In order to correct for the radioactive decay between the time the sample was collected and the time at which Rn^{222} concentration was measured, the results were corrected using a decay correction factor (DCF) which is a simple exponential function (Eq. 1) adapted from DurrIDGE RADH20 Owner's Manual (2012). Initial Rn^{222} concentrations at time of sampling can be calculated based on the following formula:

$$C_{\text{Rn}} = \frac{C_M \cdot \exp^{\frac{t}{132.4}}}{1\,000} \quad (1)$$

Where C_{Rn} is the corrected Rn^{222} concentration ($\text{Bq}\cdot\text{L}^{-1}$), C_M is the Rn^{222} concentration measured by the RAD-7 detector ($\text{Bq}\cdot\text{m}^{-3}$), \exp refers to the exponential function and t is the time since the sample was collected (hours).

RESULTS AND DISCUSSION

The results from this study suggest that Rn^{222} enriched groundwater discharges into both the Gevonden and Molenaars rivers. Less than 15% of the surface water sampled from the Gevonden and Molenaars rivers had Rn^{222} ranging between 1 and 20 $\text{Bq}\cdot\text{L}^{-1}$ (Fig. 3). Studies conducted in other rivers in various geologies around the world have found relatively low Rn^{222} concentrations typically ranging between 0.3 and 20 $\text{Bq}\cdot\text{L}^{-1}$ (Hall et al., 1985; Ellins et al., 1990; Wu et al., 2004; Schubert et al., 2008). During both wet and dry seasons, Rn^{222} ranged between 1 and 118.8 $\text{Bq}\cdot\text{L}^{-1}$ (Table A1, Appendix). Rn^{222} concentrations were considerably higher at suspected groundwater discharge sites along the rivers and would decrease substantially further away from these sites as Rn^{222} gases

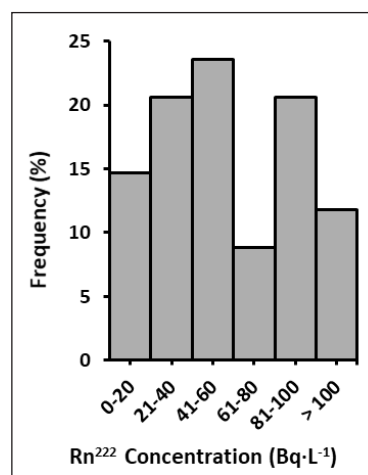


Figure 3. The frequency of Rn^{222} concentrations measured in the Gevonden and Molenaars rivers

escape into the atmosphere. A recent study conducted in South African rivers in Gauteng Province by Masevhe et al. (2017), found low Rn^{222} concentrations ranging between 0.13 and 2.87 $\text{Bq}\cdot\text{L}^{-1}$. The median Rn^{222} concentration in the Gevonden River is 76.4 $\text{Bq}\cdot\text{L}^{-1}$ and 67.2 $\text{Bq}\cdot\text{L}^{-1}$ in the dry and wet seasons, respectively (Table 1). With median Rn^{222} concentrations of 38.5 $\text{Bq}\cdot\text{L}^{-1}$ and 39.8 $\text{Bq}\cdot\text{L}^{-1}$ in the dry and wet seasons, respectively, the Molenaars River also exceeds typical Rn^{222} concentrations measured in rivers in other studies (Ellins et al., 1990; Schubert et al., 2008).

Under ambient (no pumping) conditions, Rn^{222} concentrations in groundwater range from 130–270 $\text{Bq}\cdot\text{L}^{-1}$ (Table 2). These are very high concentrations compared to groundwater samples from other global studies, which found Rn^{222} concentrations as low as 12 $\text{Bq}\cdot\text{L}^{-1}$ measured in the United Kingdom (Mullinger et al., 2007), 112.6 $\text{Bq}\cdot\text{L}^{-1}$ measured in Transylvania in Romania (Cosma et al., 2008), 26.6 $\text{Bq}\cdot\text{L}^{-1}$ detected in the volcanic regions of Spain (Moreno et al., 2014) and 16.1 $\text{Bq}\cdot\text{L}^{-1}$ in northern India (Singh et al., 2018). The use of Rn^{222} isotopes may not have been the most appropriate method in those studies due to the low concentrations detected. At our study site, slightly lower concentrations were detected at roughly 125 m, which may be attributed to a different fracture network contributing to the flow of water resulting in a decrease in Rn^{222} . Note the low concentration measured at 35 m closer to the surface where degassing may have occurred.

When the borehole was pumped and purged, the water entering the pump from the surrounding aquifer was sampled, and even higher Rn^{222} concentrations (391–593 $\text{Bq}\cdot\text{L}^{-1}$) were measured (Fig. 4). Generally, Rn^{222} concentrations in the pumped groundwater further increased during the wet season, probably due to active movement of water within the aquifer after being recharged and thus transporting Rn^{222} gases through the aquifer. It is likely that the Waterkloof Fault, on which the Gevonden and Molenaars rivers intersect, is the primary transfer mechanism for Rn^{222} gases to be mobilized by groundwater moving between U^{238} and Ra^{226} deposits within the TMG and released into the rivers via groundwater

Table 1. The variation in Rn^{222} concentrations in surface water samples in Rawsonville, South Africa

River	Season	N	Median	Min.	Max.
Gevonden	Dry	13	76.4	1	118.8
	Wet	12	67.2	33.5	104.9
Molenaars	Dry	4	38.5	36	43
	Wet	5	39.8	29.6	41.5

Table 2. Ambient Rn^{222} concentrations in groundwater samples during the dry season

Borehole depth (m)	Rn^{222} ($\text{Bq}\cdot\text{L}^{-1}$)
35	130
65	222
80	242
105	270
125	237
160	264

discharge points, which was particularly evident in the Gevonden River where very high Rn^{222} concentrations were measured and decreased as the river flowed away from the fault. Similarly, Rn^{222} concentrations in the Molenaars River spiked as it flowed over the Waterkloof Fault (see MR_29 in Table A1, Appendix).

Other hydrogeological studies conducted within regions underlain by granitic geologies and along faults also measured high Rn^{222} concentrations. For example, concentrations in the range of $2.1\text{--}653.5\text{ Bq}\cdot\text{L}^{-1}$ was measured in the Himalayas, India (Choubey et al., 2007), with $0.99\text{--}226.74\text{ Bq}\cdot\text{L}^{-1}$ measured along the North Anatolian Fault in Turkey (Akkaya et al., 2016) and $0.6\text{--}346\text{ Bq}\cdot\text{L}^{-1}$ was measured in the north-eastern region of Spain (Moreno et al., 2018). In the Karoo Basin in South Africa, a study by Eilers et al. (2015) found Rn^{222} concentrations in groundwater ranging between $<10\text{--}163\text{ Bq}\cdot\text{L}^{-1}$ while Botha et al. (2019) found that 78% of their groundwater samples had Rn^{222} concentrations below $60\text{ Bq}\cdot\text{L}^{-1}$. Both these studies found considerably lower Rn^{222} concentrations than we had measured in our study in the TMG.

Since the majority of the river samples had high Rn^{222} concentrations, with roughly 12% of samples exceeding $100\text{ Bq}\cdot\text{L}^{-1}$, it is suggested that Rn^{222} -enriched groundwater discharged into the Gevonden and Molenaars rivers, leading to an increase in Rn^{222} detected. Ellins et al. (1990) and Cook et al. (2003) found similar results which indicated an instant increase in Rn^{222} concentrations in the immediate areas surrounding groundwater discharge points into rivers. Therefore, this study suggests that Rn^{222} may be applied as a useful, natural radioactive isotope to determine groundwater discharge into surface water bodies in highly fractured aquifer systems such as the TMG. Furthermore, there is potential to use the Rn^{222} concentration measurements to estimate groundwater flow volumes, both within the borehole as well as rate of groundwater discharge into surface water, improving our understanding of groundwater–surface water interaction in complex systems such as the TMG (Schubert et al., 2011; Kafri, 2001).

CONCLUSIONS

Very high Rn^{222} concentrations were measured in the Gevonden and Molenaars rivers due to Rn^{222} -enriched groundwater discharging into the rivers. Groundwater in this region has extremely high Rn^{222} concentrations (well above the global average) due to the underlying geology and proximity of nearby faults. This case study illustrates and verifies the application of Rn^{222} isotopes as an environmental tracer in the assessment of groundwater–surface water interaction. It is particularly useful to apply in similar highly fractured aquifer systems such as the TMG. These radioactive isotopes have many of the required characteristics of an ideal environmental tracer, i.e., easily detectable in trace concentrations, chemically stable or inert for the required period of time, not typically found in large concentrations in surface water, present in most geological substrates and more importantly not filtered, absorbed nor adsorbed by the medium through which the water travels (Davis et al., 1980; Cecil and Green, 2000; Wu et al., 2004).

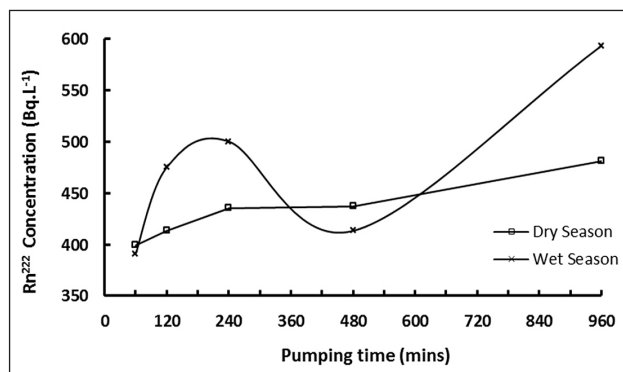


Figure 4. Rn^{222} concentrations in groundwater samples under pumping conditions

Future studies could use Rn^{222} isotopes in order to quantify groundwater influx into surface water, or vice versa, in order to promote the sustainable utilization of these water resources within the TMG region, which has gained particular focus in recent years due to the 2015–2017 drought in the Western Cape. However, we suggest that future studies invest in a high-intensity sampling campaign with increased sampling, both in groundwater and the river, in order to improve estimates and analytical rigour as well as provide greater detail on spatial variation of Rn^{222} concentrations along specific river reaches.

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APPENDIX

Table A1. A summary of Rn²²² concentrations, EC and pH in surface water samples. # represents the point at which the Molenaars River flows over the Waterkloof Fault

Sample code	GPS coordinates		River	Season	Rn ²²² (Bq·L ⁻¹)	EC (μS·cm ⁻¹)	pH
GR_1	19° 14.719' E	33° 43.145' S	Gevonden	Dry	3.3	24	5.5
				Wet	104.93	27.4	6.53
GR_2*	19° 14.713' E	33° 43.184' S	Gevonden	Dry	99.2	24	5.5
GR_3*	19° 14.712' E	33° 43.181' S	Gevonden	Dry	4.6	24	5.6
GR_4	19° 14.714' E	33° 43.186' S	Gevonden	Dry	97.8	24	5.6
				Wet	103.57	24.4	6.7
GR_5	19° 14.723' E	33° 43.112' S	Gevonden	Dry	1	23	5.5
				Wet	96.41	24.95	5.69
GR_6*	19° 14.722' E	33° 43.103' S	Gevonden	Dry	118.8	27	5.6
GR_7	19° 14.728' E	33° 43.075' S	Gevonden	Dry	2.3	24	5.3
				Wet	86.01	25.5	7.37
GR_8*	19° 14.726' E	33° 43.067' S	Gevonden	Dry	103.9	27	5.6
GR_9	19° 14.730' E	33° 43.058' S	Gevonden	Dry	94.4	26	5.7
				Wet	85.65	24.77	5.85
GR_10	19° 14.753' E	33° 43.024' S	Gevonden	Dry	3.9	24	5.6
				Wet	74.54	24.7	5.48
GR_11	19° 14.760' E	33° 42.992' S	Gevonden	Dry	85.4	26	5.7
				Wet	59.85	16.8	5.61
GR_12*	19° 14.755' E	33° 42.983' S	Gevonden	Dry	76.4	24	5.5
GR_13*	19° 14.759' E	33° 42.969' S	Gevonden	Dry	76	26	5.2
GR_21*	19° 14.778' E	33° 42.932' S	Gevonden	Wet	54.89	17	5.78
GR_22*	19° 14.809' E	33° 42.885' S	Gevonden	Wet	50.19	25.63	5.93
GR_23*	19° 14.917' E	33° 42.847' S	Gevonden	Wet	47.30	27	6.07
GR_24*	19° 14.934' E	33° 42.847' S	Gevonden	Wet	46.15	27.85	5.89
GR_25*	19° 14.994' E	33° 42.861' S	Gevonden	Wet	33.46	28.1	6.28
MR_26*	19° 9.021' E	33° 43.351' S	Molenaars	Dry	36	33	6.9
				Wet	29.58	32.03	7.7
MR_27	19° 14.052' E	33° 42.323' S	Molenaars	Dry	39	32	6.3
				Wet	40.47	25.5	7.72
MR_28	19° 14.656' E	33° 42.601' S	Molenaars	Dry	38	32	6.3
				Wet	41.52	24.5	8.01
MR_29#	19° 15.152' E	33° 42.776' S	Molenaars	Dry	43	31	6.2
				Wet	39.82	25.4	9.07
MR_30	19° 10.179' E	33° 43.425' S	Molenaars	Wet	32.98	24.7	7.99

EC – electrical conductivity, *Does not have a corresponding seasonal sample